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(12) **Patent:** (11) **CA 1116548**

Application Number: (21) **264946**

(54) METHOD OF PRODUCING A COMPOSITE COATED STEEL SHEET

(54) METHODE DE PRODUCTION D'UNE TOLE D'ACIER COMPOSITE ENDUITE

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(30) Application priority data:

Application No.	Country	Date
131425/75	Japan	Nov. 4 , 1975

Availability of licence: **N/A**

Language of filing: **English**

ABSTRACT:

ABSTRACT OF THE DISCLOSURE Coated steel sheets are provided in which the coating provides corrosion resistance and is of substantially uniform thickness, the coating is formed by dipping the steel sheet into a suspension comprising at least one substance selected from the group consisting of a water soluble organic polymer resin, a water-dispersible organic polymer resin and a water-dispersible sol of a metal compound, together with an infusible powder of a water-insoluble polymer resin, removing the coated steel sheet from the suspension and curing the coated composite by heat treatment. In certain cases, a metal powder, a metal alloy powder or a powder of a difficultly water-soluble or water-insoluble metal compound may be included in the suspension to improve the corrosion resistance.

CLAIMS: Show all claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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264946

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ABSTRACT OF THE DISCLOSURE 1116548

Coated steel sheets are provided in which the coating provides corrosion resistance and is of substantially uniform thickness, the coating is formed by dipping the steel sheet into a suspension comprising at least one substance selected from the group consisting of a water-soluble organic polymer resin, a water-dispersible organic polymer resin and a water-dispersible sol of a metal compound, together with an infusible powder of a water-insoluble polymer resin, removing the coated steel sheet from the suspension and curing the coated composite by heat treatment. In certain cases, a metal powder, a metal alloy powder or a powder of a difficultly water-soluble or water-insoluble metal compound may be included in the suspension to improve the corrosion resistance.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A method of producing a composite coated steel sheet which comprises

electrolytically treating a steel sheet in a suspension comprising

i) at least one substance selected from the group consisting of a water-soluble resin, and a water-dispersible resin;

ii) a water-dispersible sol of a metal compound; and

iii) an infusible organic polymer resin powder;

removing a coated steel sheet from the suspension and curing the coated steel sheet by heat treatment.

2. A method according to claim 1, wherein the resin in i) is selected from the group consisting of epoxy resins, phenol resins, alkyl resins, acrylic resins and butadiene resins and is present in the suspension in an amount of from about 2 to 50 g/l.

3. A method according to claim 1, wherein the metal compound in ii) is selected from the group consisting of an oxide or hydroxide of a metal selected from the group consisting of nickel, titanium, chromium, zinc, aluminum and tin; said metal compound having a particle size of about 1 to 500 mμ, and being present in said suspension in an amount from about 1 to 100 g/l.

4. A method according to claim 1 or 2, wherein the infusible organic polymer resin powder is selected from the group consisting of nylon, polyethylene, polypropylene, polyamides, diacryl phthalate, ethylene-vinyl acetate copolymer resins, cellulose acetate butyrate, polyurethanes, polystyrene,

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polycarbonates, chlorovinyl resins, polyfluorovinyl resins, epoxy resins or acrylic resins; said resin powder having an average particle diameter of under 200 μ.

5. A method according to claim 1 or 2, wherein said treating is carried out at a temperature of about 10 to about 70°C.

6. A method according to claim 1, wherein the steel sheet is treated cathodically for a low pH and anodically for a high pH.

7. A method according to claim 1 or 2, wherein said steel sheet is a plated steel sheet.

8. A method of producing a composite coated steel sheet which comprises electrolytically treating a steel sheet in a suspension comprising:

i) at least one substance selected from the group consisting of a water-soluble resin, and a water-dispersible resin;

ii) a water-dispersible sol of a metal compound;

iii) an infusible organic polymer resin powder; and

iv) at least one member selected from the group consisting of a metal powder, a metal alloy powder and a difficultly water-soluble or water-insoluble powdered metal compound, being present in said suspension at a concentration not less than 3 g/l; removing the coated metal sheet from the suspension and then curing the coated metal sheet by heat treatment.

9. A method according to claim 8, wherein the infusible organic polymer resin powder is selected from the group consisting of nylon, polyethylene, polypropylene, polyamides, diacryl phthalate, ethylene-vinyl acetate copolymer resins,

cellulose acetate butyrate, polyurethanes, polystyrene, polycarbonates, chlorovinyl resins, polyfluorovinyl resins, epoxy resins and acrylic resins; said infusible polymer resin powder having an average particle diameter of less than 200 μ.

10. A method according to claim 8, wherein iv) is a metal powder selected from the group consisting of aluminum, zinc, chromium, cobalt, iron, nickel, tin, lead, copper, manganese, titanium, molybdenum, zirconium, bismuth, antimony and tungsten; said metal powder having an average particle diameter of less than 200 μ.

11. A method according to claim 8 wherein iv) is a metal alloy powder of two or more metals selected from the group consisting of aluminum, zinc, chromium, cobalt, nickel, iron, tin, lead, copper, manganese, titanium, molybdenum, zirconium, bismuth, antimony and tungsten; said metal alloy powder having an average particle diameter of less than 200 μ.

12. A method according to claim 8, wherein iv) is a difficultly water-soluble or water-insoluble powdered compound of a metal selected from the group consisting of aluminum, zinc, chromium, cobalt, nickel, iron, tin, lead, copper, manganese, titanium, molybdenum, zirconium, bismuth, antimony or tungsten; said powdered metal compound having an average particle diameter of less than 200 μ.

The present invention relates to a method of producing a coated steel sheet; a coated steel sheet product and a coating composition; more particularly, the invention comprises a method in which a steel sheet is electrolytically treated in a suspension, and the resulting coating on the sheet is cured by heat treatment.

Methods are known for producing a coated metal sheet, by use of a polymer resin; such methods may be summarized as follows:

1. By the method of roller coating, knife coating, spray coating and immersion coating, an organic solvent-type paint is coated on the metal sheet and then is cured by heat treatment.

2. By the above-mentioned coating method, a mixture of polymer resin powder and adhesive solution is coated on the steel sheet, and then is cured by heat treatment.

3. By the method of injection coating, a polymer resin powder is coated on the metal sheet.

4. By the method of electrophoresis coating, a metal sheet is coated with an organic solvent containing a polymer resin powder, is dried and is then cured by heat treatment.

5. By the method of electrophoresis coating, a metal sheet is coated with a treatment solution containing a water-dispersible polymer resin and is then cured by heat treatment.

6. By the method of electrostatic coating, a polymer resin powder is coated on a metal sheet, and is then cured by heat treatment.

In the above coating methods 1, 2 and 3, it is difficult to control the thickness or uniformity of the coating. Uniformity of the coating thickness with regard to quality control is often one of the most difficult factors to achieve. Also, for the application of a thin coating thickness, the methods are very disadvantageous from an economical standpoint. Further, when powders

of a polymer resin and inorganic compound are used as coating materials, these methods become more and more difficult.

In the case of methods 1, 2 and 4, wherein an organic solvent is used, a public nuisance is caused by the use of such solvent.

Method 5 requires that a strong ionic charge be produced by dissociation of the polymer resin. Therefore, the polymer resin used must be carefully chosen. For example, insoluble nylon, polyethylene and others cannot be electrodeposited by the method of 5.

Method 6 has the disadvantage that adhesion of the resin powder is poor and the coated powder is often easily separated from the base metal sheet by slight impact or contact after production. In cases where the coating contains metal powder, the coating adhesion deteriorates further.

On the other hand, according to Japanese patent laid-open No. Sho 50-75623,(June 20, 1975, Japan, K. Ariga et al.), a metal sheet is cathodically electrotreated in a suspension consisting of alumina sol of 1 to 500 mμ (particle diameter) with a positive electric charge and an organic polymer resin. By employing this method, one can easily control the coating thickness by controlling the amount of electricity. It is not necessary to use harmful organic solvents, therefore, a public nuisance is not caused by the treatment solution. Also, the above-mentioned insoluble nylon, polyethylene, etc. and inorganic powder can easily be electrodeposited in the suspension as described above.

The present invention provides an improvement in the coating adhesion in coated sheets of the kind described in the aforementioned Japanese patent laid-open No. Sho 50-75623.

The present invention involves coating a steel plate

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with composite materials, which steel plate is electrotreated in a suspension, which contains

i) at least one substance selected from the group consisting of a water-soluble resin, and a water dispersible resin;

ii) a water-dispersible sol of a metal compound; and

iii) an infusible organic polymer resin powder; and further including in certain cases; and

iv) a metal powder, metal alloy powder or a difficultly water-soluble or water-insoluble powdered metal compound.

It is an object of the present invention to produce a steel sheet coated with a composite material containing

i) at least one substance selected from the group consisting of a water-soluble resin and a water-dispersible resin;

ii) a water dispersible sol of a metal compound; and

iii) an infusible organic polymer resin powder; and in some cases;

iv) a metal powder, metal alloy powder or a difficultly water-soluble or water-insoluble powdered metal compound; which product has excellent corrosion resistance because of the uniform coating with the composite material.

According to the invention, there is provided a method of producing a composite coated steel sheet which comprises:

electrolytically treating a steel sheet in a suspension comprising:

i) at least one substance selected from the group consisting of a water-soluble resin, and a water-dispersible resin;

ii) a water dispersible sol of a metal compound; and

iii) an infusible organic polymer resin powder, removing a coated steel sheet from the suspension, and

curing the coated steel sheet by heat treatment.

According to another aspect of the invention, there is provided a method of producing a composite coated steel sheet which comprises electrolytically treating a steel sheet in a suspension comprising:

i) at least one substance selected from the group consisting of a water-soluble resin, and a water-dispersible resin;

ii) a water-dispersible sol of a metal compound;

iii) an infusible organic polymer resin powder; and

iv) at least one member selected from the group consisting of a metal powder, a metal alloy powder and a difficultly water-soluble or water-insoluble powdered compound of a metal, being present in said suspension at a concentration not less than 3 g/l; removing a coated steel sheet from the suspension and then curing the coated metal sheet by heat treatment.

According to a further aspect of the invention there is provided a coated steel sheet, comprising a steel sheet substrate having a corrosion resistant thermally cured coating comprising:

i) at least one substance selected from the group consisting of a water-soluble resin, and a water-dispersible resin;

ii) a water-dispersible sol of a metal compound; and

iii) an infusible organic polymer resin powder.

According to a still further aspect of the invention, there is provided a coating composition for producing thermally cured corrosion resistant coatings comprising in a liquid medium

i) at least one substance selected from the group consisting of a water-soluble resin, and a water-dispersible resin;

ii) a water-dispersible sol of a metal compound; and

iii) an infusible organic polymer resin powder.

The liquid medium is suitably an aqueous medium, for example, water.

The water-soluble or water-dispersible organic polymer resin which is one of the main components of the coating has the effect of improving the coating adhesion. Such resins include, by way of example, phenol-type resins, alkyd-type resins, epoxy-type resins, acrylic-type resins and butadiene-type resins. The particle diameter of these resins is suitably under 1μ. A particle diameter of more than 1μ is unfavourable because it results in a deterioration in appearance of the deposited surface.

The above polymer resin is suitably employed in a concentration in the range of 2 to 50 g/l (as solid) in order to improve the coating adhesion. A concentration of less than 2 g/l has little effect on the coating adhesion and on the other hand, a concentration of more than 50 g/l has a remarkably bad influence on the throwing power.

The water-dispersible sol may suitably comprise an oxide or hydroxide of a metal, for example, zinc, tin, chromium, nickel, titanium, zirconium and aluminum. The diameter of the sol particle is suitably 1 to 500 mμ; and the sol is suitably employed in a concentration in the range of 1 to 100 g/l. The treatment suspension may contain one or more of such sols. If the concentration of the water-dispersible sol is less than 1 g/l, the advantageous effects are not fully realized. At a concentration of more than 100 g/l, the improvement in film-forming is not in proportion to the increased concentration; and in fact it disappears because if the viscosity of the suspension becomes too high, the solution becomes difficult to work with.

Almost any infusible powder of an organic polymer resin can be used for the suspension of the present invention, but it is required that the above-mentioned powder not be substantially reactive in the electrolytic solution.

For example, there may be used nylon, polyethylene,

polypropylene, polyamides, diacryl phthalate, ethylene-vinyl acetate copolymer resins, cellulose acetate butyrate, polyurethanes, polystyrene, polycarbonates, chlorovinyl resins, polyfluorovinyl resins, epoxy resins and acrylic resins. The treatment solution can contain one or more of these powder resins.

The particle size of the infusible powder tends to influence the appearance of the coating layer and the coating adhesion. Small size powder particles form a close deposit layer, whereas, large size powder particles produce a porous deposit layer and poor coating adhesion. However, these defects can be overcome by treatment with a rolling press after electrodeposition or heat treatment. Therefore, although the powder size is not specifically restricted, it is desirable that it be under 200μ in order to facilitate the production of a satisfactory coating.

The concentration of the infusible powder in the treatment solution depends on the powder size, the kind of powder and the combination of materials.

A concentration of less than 3 g/l tends to decrease the current efficiency.

For the purpose of further improving corrosion resistance, there may optionally be included in the suspension at least one powder selected from metals, alloys and difficultly water-soluble or water-insoluble compounds of the metals.

The metal powders include, by way of example, aluminum, zinc, chromium, cobalt, nickel, iron, tin, lead, copper, manganese, titanium, molybdenum, zirconium, bismuth, antimony and tungsten. Alloy powders, include, by way of example, the alloys of the aforementioned metals. Difficultly water-soluble or water-insoluble powder compounds include, by way of example, compounds of the aforementioned metals, for example, the hydride, sulfide,

chloride, oxide, sulfate, nitrate, hydroxide and carbide.

The suspension can contain one or more of these powders, suitably having a particle size (diameter) of under 200μ. A diameter of more than 200μ produces poor results such as decrease in the formability and appearance of coating layer and deterioration of the corrosion resistance.

The concentration of inorganic powder depends on the particle size of the powder, the kind of powder and the combination of materials, as in the case of the polymer resin powder.

At a concentration of less than 3 g/l, improvement in corrosion resistance is not obtained.

The steel sheet is suitably treated with the suspension at a temperature of 10-70°C. At a temperature higher than 70°C, it is difficult to keep the concentration of the bath constant because of high evaporation.

The current density for the electrolytic treatment is not especially restricted, but it must be increased for a short period of time in order to obtain an increase in the coating thickness.

On electroplating, the polarity of the metal sheet treated depends upon the composition of the suspension. In general, when the pH of the treatment solution is on the acid side, the metal is cathodically treated. On the other hand, when the pH of the solution is on the alkaline side, the metal sheet is anodically treated.

Agitation during electrotreatment has a tendency to decrease the deposit efficiency, but some agitation is desirable in order to uniformly maintain the powder particles in the suspension.

Surface active agents or alcohol may also be added to

the treatment solution in order to uniformly disperse the powder in the treatment solution. For example, nylon powder (diameter: 50μ) can uniformly and quickly be mixed by the addition of 1 g/l of an alkyl betaine-type surface active agent.

After preparation of the suspension by the above-mentioned method, the metal sheet is cathodically or anodically treated in the suspension.

The electrodeposited layer formed on the metal sheet can be rinsed with water and then dried.

The coated metal sheet formed by the above-mentioned method is cured by heat treatment. The conditions of the heat treatment depend on the kind of powder and coating thickness. At any rate it is required that the resin powder be brought into the molten state. Also before or after curing, a pressure rolling treatment is desirable in order to improve the appearance of the coated sheet.

The present invention is applicable to the surface treatment of various metal sheets and other metal shapes. For example, steel sheets, steel sheets electrotreated in a chromate solution, steel sheets plated with chromium, tin, zinc, nickel, aluminum and other metal or with alloys of these metals. Also the present invention is applicable to those steel sheets which have been subjected to a treatment such as with a chromate or phosphate.

The invention is further illustrated by reference to the following examples which are not intended to be construed as limiting.

EXAMPLE I

A low carbon steel sheet of 0.5 mm thickness, after annealing and temper rolling, was cleaned in 70 g/l of sodium hydroxide solution at a temperature of 70°C for 10 seconds, rinsed with

water and then placed in 70 g/l of sulfuric acid for 5 seconds at 20°C and again rinsed with water. The pre-treated steel sheet was

immediately treated by the method of the present invention.

Treatment of the present invention:

Bath composition

hydroxide sol of chromium	(average diameter of particles:100mμ) 35 g/l
epoxy powder (average diameter:40μ)	10 g/l
polyacrylamide (water-soluble resin)	10 g/l
Temperature	20°C
Current density (cathodic treatment)	5 A/dm^2
Plating time	15 seconds

The coated metal sheet thus obtained was blue in colour. The coated sheet was heated for 2 minutes at a temperature of 250°C and a light blue coated steel sheet having a coating thickness of 14μ was obtained. An Erichsen test indicated an 8 mm depth. The coated sheet showed no evidence of adhesion loss of the coated layer. The coated sheet was subjected to a corrosion test (salt spray test) according to JIS (Japanese Industrial Standard) Z 2371 and the coated sheet did not show any red rust after 200 hours.

On the other hand, in a separate sample produced in the same way but omitting the polyacrylamide, a red rust was observed after 200 hours in the salt spray test.

By way of further comparison a steel sheet coated with epoxy powder was produced by the conventional method of spray coating; the interface adhesion between the coating and the base metal was poor and the powder was separated from the base metal by slight impact. The epoxy powder was baked carefully so as to not separate from the base metal, but even so the coated sheet obtained showed red rust after 10 hours in the aforementioned corrosion test.

EXAMPLE II

The same low carbon steel sheet was subjected to the same pre-treatment as described in Example I. After that, the pre-treated sheet was immediately treated by the method of the present invention.

Treatment of the present invention:

Bath composition

hydroxide sol of chromium (average diameter of particles:100mμ)	35 g/l
epoxy powder (average diameter:40μ)	10 g/l
polyacrylamide (water-soluble resin)	10 g/l
zinc powder (diameter:100μ)	100 g/l
Temperature	20°C
Current density (cathodic treatment)	5 A/dm^2
Plating Time	15 seconds

The coated sheet thus obtained was gray in colour. The coated sheet was heated for 2 minutes at a temperature of 250°C and a gray coated sheet having a coating thickness of 14μ was obtained.

The Erichsen test showed an 8 mm depth and the coated sheet showed no evidence of adhesion loss of the coating layer. The coated sheet was evaluated by the salt spray test as described in Example I. The results show that no red rust was observed after 500 hours and that the addition of zinc powder was effective for improving the corrosion properties.

On the other hand, a steel sheet coated with epoxy powder only by the conventional method of spray coating had inferior interface adhesion between the powder and base metal. The epoxy powder was baked carefully so as not to separate from the base steel, but even so the coated sheet obtained showed a red rust after 24 hours.

EXAMPLE III

The same low carbon steel sheet as described in Example I was electrogalvanized (weight of deposit:10 g/m^2), and then treated by a chromate method. It was then treated as follows:

Treatment of the present invention:

Bath composition

butadiene-type water soluble resin	20 g/l
epoxy powder (average diameter:40μ)	10 g/l
zinc powder (average diameter:100μ)	100 g/l
Temperature	20°C
Current density (anodic treatment)	5 A/dm^2
Plating time	15 seconds

The coated sheet thus obtained was gray in colour. The coated sheet was baked for 30 seconds at a temperature of 400°C. The results obtained showed that the gray coated sheet had a coating thickness of 20μ.

The coated sheet was evaluated by the coating adhesion and corrosion resistance tests described in Example II. The results show excellent properties as described in Example II.